

IN THE CLAIMS

RECEIVED  
CENTRAL FAX CENTER

APR 05 2007

1-27 (canceled)

28. (currently amended) ~~The polyurethane-polymer hybrid dispersion of claim 26-A~~  
polyurethane-polymer hybrid dispersion prepared by a process comprising the steps of:

a) preparing a dispersion component or binder component based on an aqueous solution  
or dispersion of an optionally hydroxy- or amino-functional polyurethane-polymer hybrid having  
fluorinated or unfluorinated side chains, by

a.) admixing 5 to 100 parts by weight of a laterally fluorine-modified, anionically  
stabilized polyurethane base dispersion (A) having, a polymer-bonded fluorine content of up to  
5% by weight, at least one of a hydroxyl number of amine number of 0 to 250 mg KOH/g, a  
solids content of 20% to 60% by weight, a solvent content of 0 to 20% by weight, and a number  
average molecular weight of 5,000 to 100,000 daltons with 3 to 300 parts by weight of a  
monomer component (B) comprising

(i) 1 to 100 parts by weight of one or more unsaturated monomers (B)(i) having one or  
more free-radically polymerizable double bonds, selected from the group consisting of acrylic  
acid, methacrylic acid, styrene, and derivatives thereof, or

(ii) 1 to 100 parts by weight of one or more unsaturated fluorine-modified monomers  
(B)(ii) having one or more free-radically polymerizable double bonds, selected from the group  
consisting of an alkyl (per)fluoro (meth)acrylate, a (per)fluoroalkyl (meth)acrylate a  
(per)fluoroalkyl (per)fluoro(meth)acrylate, a reaction product of 1-(1-isocyanato-1-methylethyl)-  
3-(2-propenyl)benzene (m-TMI) and a perfluoroalkyl alcohol, or

(iii) 1 to 100 parts by weight of one or more unsaturated optionally fluorine-modified  
monomers (B)(iii) having one or more free-radically polymerizable double bonds, selected from

the group consisting of polyhedral oligomeric polysilsesquioxanes (POSS) of the formula  $(RSiO_{1.5})_n$  with n = 4, 6, 8, 10, 12; and R is an organic radical having 1 to 100 C atoms and 0 to 50 N, 0 to 50 O, or 0 to 50 F, 0 to 50 Si or 0 to 50 S atoms and a number average molecular weight of 250 to 25,000 daltons,

with 0.01 to 10 parts by weight of an initiator component (C), comprising at least one lipophilic free-radical initiator having one or more thermally labile azo or peroxy groups, and 0 to 200 parts by weight of water, wherein the monomer component (B), the initiator component (C), and the water may optionally be metered in simultaneously, successively or as a mixture to the polyurethane base dispersion (A), and subsequently

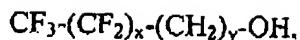
a<sub>2</sub>) conducting, in the reaction mixture from stage a<sub>1</sub>), as a result of the thermal decomposition of component (C), a free-radical polymerization of component (B) within micelles of the polyurethane base dispersion (A),

and, optionally,

b) subsequently reacting the dispersion or binder component formed from components (A) to (C) from stage a<sub>2</sub>) with 20 to 100 parts by weight of a crosslinker component (D) (curing agent), wherein said crosslinker component or curing agent (D) is a water-dispersible polyisocyanate having at least one of an aliphatically, cycloaliphatically, or aromatically attached isocyanate group, wherein the polyisocyanate may optionally contain from 0 to 25% by weight of an organic solvent,

wherein component (A) is a polyurethane dispersion which contains as structural groups laterally fluorine-modified macromonomers based on a reaction product of

- a) a perfluoroalkyl alcohol, a diisocyanate, or diethanolamine, a perfluoroalkyl alcohol having terminal methylene groups of {hydrocarbon spacers} the formula

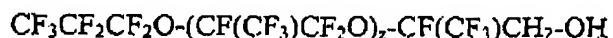


wherein

x is from 3-20 and

y is from 1-6

or a hexafluoropropene oxide (HFPO) oligomer alcohol of the formula,

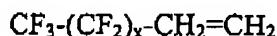


wherein

Z is from 1-10,

or a mixture of thereof, or

b) a perfluoroalkylalkene and diethanolamine, or a perfluoroalkylalkene having terminal a methylene group (hydrocarbon spacer) of the formula



wherein

x is from 3-20

or a mixture thereof, or

c) an alkyl (per)fluoro(meth)acrylate, a (per)fluoroalkyl (meth)acrylate, a (per)fluoroalkyl (per)fluoro(meth)acrylate and diethanolamine, or

d) a (per)fluoroalkylalkene oxide N-methylethanolamine or diethanolamine.

29. (currently amended) ~~The polyurethane polymer hybrid dispersion of claim 26 A~~  
~~polyurethane-polymer hybrid dispersion prepared by a process comprising the steps of:~~

a) preparing a dispersion component or binder component based on an aqueous solution or dispersion of an optionally hydroxy- or amino-functional polyurethane-polymer hybrid having fluorinated or unfluorinated side chains, by

a) admixing 5 to 100 parts by weight of a laterally fluorine-modified, anionically stabilized polyurethane base dispersion (A) having, a polymer-bonded fluorine content of up to 5% by weight, at least one of a hydroxyl number of amine number of 0 to 250 mg KOH/g, a solids content of 20% to 60% by weight, a solvent content of 0 to 20% by weight, and a number average molecular weight of 5,000 to 100,000 daltons with 3 to 300 parts by weight of a monomer component (B) comprising

(i) 1 to 100 parts by weight of one or more unsaturated monomers (B)(i) having one or more free-radically polymerizable double bonds, selected from the group consisting of acrylic acid, methacrylic acid, styrene, and derivatives thereof, or

(ii) 1 to 100 parts by weight of one or more unsaturated fluorine-modified monomers (B)(ii) having one or more free-radically polymerizable double bonds, selected from the group consisting of an alkyl (per)fluoro (meth)acrylate, a (per)fluoroalkyl (meth)acrylate a (per)fluoroalkyl (per)fluoro(meth)acrylate, a reaction product of 1-(1-isocyanato-1-methylethyl)-3-(2-propenyl)benzene (m-TMI) and a perfluoroalkyl alcohol, or

(iii) 1 to 100 parts by weight of one or more unsaturated optionally fluorine-modified monomers (B)(iii) having one or more free-radically polymerizable double bonds, selected from the group consisting of polyhedral oligomeric polysilsesquioxanes (POSS) of the formula  $(RSiO_{1.5})_n$  with n = 4, 6, 8, 10, 12; and R is an organic radical having 1 to 100 C atoms and 0 to 50 N, 0 to 50 O, or 0 to 50 F, 0 to 50 Si or 0 to 50 S atoms and a number average molecular weight of 250 to 25,000 daltons,

with 0.01 to 10 parts by weight of an initiator component (C), comprising at least one lipophilic free-radical initiator having one or more thermally labile azo or peroxy groups, and 0 to 200 parts by weight of water, wherein the monomer component (B), the initiator component (C), and the water may optionally be metered in simultaneously, successively or as a mixture to the polyurethane base dispersion (A), and subsequently

a<sub>2</sub>) conducting, in the reaction mixture from stage a<sub>1</sub>), as a result of the thermal decomposition of component (C), a free-radical polymerization of component (B) within micelles of the polyurethane base dispersion (A),

and, optionally,

b) subsequently reacting the dispersion or binder component formed from components (A) to (C) from stage a<sub>2</sub>) with 20 to 100 parts by weight of a crosslinker component (D) (curing agent), wherein said crosslinker component or curing agent (D) is a water-dispersible polyisocyanate having at least one of an aliphatically, cycloaliphatically, or aromatically attached isocyanate group, wherein the polyisocyanate may optionally contain from 0 to 25% by weight of an organic solvent,

wherein component (B)(iii) is made a reactive polyhedral oligomeric polysilsesquioxane (POSS) of the formula  $(RSiO_{1.5})_8$  wherein R is at least one of methacryloyloxypropyl,  $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$ , a H, C<sub>1</sub>-C<sub>25</sub> alkyl, C<sub>3</sub>-C<sub>25</sub> cycloalkyl, C<sub>6</sub>-C<sub>30</sub> aryl,  $(CH_2)_3(OCH_2CH_2)_nOMe$ , aminopropyl, epoxypropyl, dimethoxysilyloxy, isocyanatopropyl, or triethoxysilylpropyl.

30. (currently amended) A polyurethane-polymer hybrid dispersion prepared by a process comprising the steps of:

a) preparing a dispersion component or binder component based on an aqueous solution or dispersion of an optionally hydroxy- or amino-functional polyurethane-polymer hybrid having fluorinated or unfluorinated side chains, by

a<sub>1</sub>) admixing 5 to 100 parts by weight of a laterally fluorine-modified, anionically stabilized polyurethane base dispersion (A) having, a polymer-bonded fluorine content of up to 5% by weight, at least one of a hydroxyl number of amine number of 0 to 250 mg KOH/g, a solids content of 20% to 60% by weight, a solvent content of 0 to 20% by weight, and a number average molecular weight of 5,000 to 100,000 daltons with 3 to 300 parts by weight of a monomer component (B) comprising

(i) 1 to 100 parts by weight of one or more unsaturated monomers (B)(i) having one or more free-radically polymerizable double bonds, selected from the group consisting of acrylic acid, methacrylic acid, styrene, and derivatives thereof, or

(ii) 1 to 100 parts by weight of one or more unsaturated fluorine-modified monomers (B)(ii) having one or more free-radically polymerizable double bonds, selected from the group consisting of an alkyl (per)fluoro (meth)acrylate, a (per)fluoroalkyl (meth)acrylate a (per)fluoroalkyl (per)fluoro(meth)acrylate, a reaction product of 1-(1-isocyanato-1-methylethyl)-3-(2-propenyl)benzene (m-TMI) and a perfluoroalkyl alcohol, or

(iii) 1 to 100 parts by weight of one or more unsaturated optionally fluorine-modified monomers (B)(iii) having one or more free-radically polymerizable double bonds, selected from the group consisting of polyhedral oligomeric polysilsesquioxanes (POSS) of the formula  $(RSiO_{1.5})_n$  with n = 4, 6, 8, 10, 12; and R is an organic radical having 1 to 100 C atoms and 0 to 50 N, 0 to 50 O, or 0 to 50 F, 0 to 50 Si or 0 to 50 S atoms and a number average molecular weight of 250 to 25,000 daltons,

with 0.01 to 10 parts by weight of an initiator component (C), comprising at least one lipophilic free-radical initiator having one or more thermally labile azo or peroxy groups, and 0 to 200 parts by weight of water, wherein the monomer component (B), the initiator component (C), and the water may optionally be metered in simultaneously, successively or as a mixture to the polyurethane base dispersion (A), and subsequently

a<sub>2</sub>) conducting, in the reaction mixture from stage a<sub>1</sub>), as a result of the thermal decomposition of component (C), a free-radical polymerization of component (B) within micelles of the polyurethane base dispersion (A),

and, optionally,

b) subsequently reacting the dispersion or binder component formed from components (A) to (C) from stage a<sub>2</sub>) with 20 to 100 parts by weight of a crosslinker component (D) (curing agent), wherein said crosslinker component or curing agent (D) is a water-dispersible polyisocyanate having at least one of an aliphatically, cycloaliphatically, or aromatically attached isocyanate group, wherein the polyisocyanate may optionally contain from 0 to 25% by weight of an organic solvent ~~The polyurethane polymer hybrid dispersion of claim 26,~~

wherein component (B)(iii) is a reactive polyhedral oligomeric polysilsesquioxane (POSS) of the formula  $(R_aX_bSiO_{1.5})_m$

wherein

a is 0 or 1,

b is 0 or 1,

a + b = 1,

m is 2, 6, 8, 10, or 12, and

R is H, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl or cycloalkynyl group or polymer unit, each of which are substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units, which are attached via a polymer unit or a bridging unit,

X is oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxyisilyl, siloxy, alkylsiloxy, alkoxyisiloxy, silylalkyl, alkoxyisilylalkyl, alkylsilylalkyl, halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine, a polyether group, or a substituent of type R containing at least one such group of type X,

wherein the substituents of type R and the substituent of type X are the same or different.

31. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein component (C) is a free-radical initiator which has a half-life of one hour at a decomposition temperature in the range from 40 to 120°C.

32. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein component (C) is 2,2'-azobis(2-methylbutyronitrile) or 2,2'-azobis(2-methylpropionitrile).

33. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the initiator/monomer molar ratio of components (B) and (C) is set at a level of 0.001 to 0.05.

34. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein in the anionically modified polyurethane hybrid polymer formed from components (A) to (C) the amount of carboxylate or sulfonate groups is set at 5 to 25 meq·(100 g)<sup>-1</sup> and the acid number at 2.5 to 15 meq KOH·g<sup>-1</sup>.

35. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the solids content in terms of fluorine-modified polyurethane hybrid polymer

consisting of components (A) to (C) is set at 30% to 70% by weight based on the total amount of the polyurethane-polymer hybrid dispersion.

36. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the ratio of the proportional solids contents of (fluorine-modified) polyurethane resin from component (A) and (fluorine-modified) polymer resin from components (B) and (C) is set at 20%:80% to 80%:20% by weight.

37. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the polyurethane dispersions or polyurethane-polymer hybrid dispersions contain less than 10% by weight of organic solvents.

38. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the average particle size of the micelles amounts to 50 to 500 nm.

39. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the average molar mass (number average) is from 50,000 to 500,000 daltons.

40. (currently amended) The polyurethane-polymer hybrid dispersion of claim 28 of claim 26, wherein the ratio of crosslinker component (D) to the binder component comprising components (A) to (C) is from 1:3 to 1:5.

41. (currently amended) A method of preparing the polyurethane-polymer hybrid dispersion of claim 28 of claim 26, comprising:

preparing a dispersion component by

a.) optionally diluting an optionally fluorine-modified polyurethane base dispersion (A) with water and admixing it with a pre-prepared mixture of components (B) and (C) and also with water, it being possible to meter in the monomer component (B) or its individual

constituents, the initiator component (C), and the water simultaneously, successively or in a mixture to the polyurethane base dispersion (A), and finally

a<sub>2</sub>) carrying out a free-radical polymerization of component (B) by means of the thermal decomposition of component (C),

and optionally, by

b) reacting the binder component formed from components (A) to (C) from stage a<sub>2</sub>) subsequently with 20 to 100 parts by weight of a crosslinker component (D).

42. (previously presented) The method of claim 41, wherein reaction stage a<sub>1</sub>) is carried out at a temperature of 15 to 35°C.

43. (previously presented) The method of claim 41, wherein reaction stage a<sub>2</sub>) is carried out at a temperature difference of  $\pm 10^\circ\text{C}$  relative to the temperature at which component (C) has a half-life of 1 hour.

44. (previously presented) The method of claim 41, wherein reaction stage a<sub>2</sub>) is carried out at a temperature of  $80 \pm 10^\circ\text{C}$  when component (C) is 2,2'-azobisisobutyronitrile.

45. (previously presented) The method of claim 41, wherein the free-radical polymerization in reaction stage a<sub>2</sub>) is carried out without further emulsifiers.

46. (previously presented) The method of claim 41 wherein reaction stage b) is carried out at a temperature of 15 to 35°C.

47. (canceled)

48. (canceled)

49. (canceled)

50. (canceled)

51. (canceled)

52. (new) The polyurethane-polymer hybrid dispersion of claim 26, wherein component (A) is an optionally hydroxy- or amino-functionalized polyurethane dispersions based on an optionally hydrophobically modified polyalkylene glycol, an aliphatic or aromatic polyester, a polycaprolactone, a polycarbonate,  $\alpha,\omega$ -polybutadienepolyol, an  $\alpha,\omega$ -polymethacrylatediol, an  $\alpha,\omega$ -dihydroxyalkylpolydimethylsiloxane, a macromonomer, a telechelic, a hydroxy-functional epoxy resin, an oxidatively drying alkyd resin based on a bisepoxide and an unsaturated fatty acid, a hydroxy-functional polysulfide or a mixture thereof.

53. (new) A method comprising utilizing the polyurethane-polymer hybrid dispersion of claim 52 in one-component or two-component form.

54. (new) The method of claim 53, wherein for a two-component application, wherein formulated or unformulated polyurethane-polymer hybrid dispersion is the binder component and a water-emulsifiable (paint) polyisocyanate is the curing component.

55. (new) The method of claim 53, wherein the dispersion is used to form a permanent oil- and water-repellent surface treatment or modification of a mineral or a nonmineral substrate.

56. (new) The method of claim 55, wherein said substrate is an  
a) inorganic surface, such as porous, absorbent, rough, and polished building material, a construction material selected from concrete, gypsum, silica or a silicate, an artificial stone, a natural stone, clay, cement, brick, an enamel, a filler, a pigment, glass, ceramic, a metal or a metal alloy, or  
b) an organic surface, such as wood, a woodbase material, wood veneer, a glass fiber-reinforced plastic (GRP), a plastic, leather, a natural fiber, a polar organic polymer or a composite material.

57. (new) A coated substrate comprising a substrate coated with a coating comprising the dispersion of claim 52, wherein said coating is at least one of

- an antigraffiti coating,
- an anti soiling coating,
- an easy to clean coating,
- a balcony coating, a roof coating, a baking varnish, an ink, a paint, a masonry paint, a floor coating, a light-, medium- or high-duty industrial floor, a car park surfacing, a sports floor, a seal,
- a prefabricated concrete component,
- a concrete molding,
- a tile or joint,
- an adhesive or sealant,
- a soundproofing for a wall,
- corrosion control,
- renders or decorative plaster,
- an exterior insulation and finishing systems (EIFS) and exterior insulation systems (EIS),
- a coating for an auto, part, a coil coating, a baking varnish, a glass frontage, a glass surface, a ceramic, a sanitary ceramic, a leather dressing, a surface-modified filler, a surface modified pigment, a paper coating, a rotor for a wind turbine, or a marine paint.